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Reaction Products of Aquatic Humic Substances with Chlorine

by J. D. Johnson,* R. F. Christman,*
D. L. Norwood* and D. S. Millington*

A major concern of the chlorination of aquatic humic materials is the ubiquitous production of trihalomethanes. A large number of other chlorinated organic compounds, however, have been shown to be formed by chlorine's reaction with humic substances. In this study, humic material was concentrated from a coastal North Carolina lake and chlorinated at a chlorine to carbon mole ratio of 1.5 at pH 12. A high pH was necessary for complete dissolution of the humic material and for production of adequate quantities of oxidation and chlorination products for extraction, separation and mass spectrometric identification. After concentration in ether, samples were methylated, separated with a 50-m OV-17 glass capillary column or a 25 m SP-2100 fused-silica column and identified. A Hewlett-Packard 5710A gas chromatograph interfaced to a VG Micromass 7070F double-focusing mass spectrometer was used. Low resolution, accurate mass measurements were made with a combined EI-CI source.

The ability to do low resolution, accurate mass measurements made possible a rapid scan function necessary for capillary column gas chromatography. Accurate mass measurements allowed increased confidence in the identification of compounds, most of which are not available as standards. The products identified in these studies were chlorinated aliphatic straight-chain acids dominated by di- and trichloroacetic acid and the chlorinated dicarboxylic acids: succinic, fumaric and maleic acids. Chlorinated and unchlorinated aliphatic mono- and dicarboxylic acids and unchlorinated polycarboxylic aromatic acids comprise the remaining bulk of the compounds identified.

Introduction

Since Rook (*1*) first suggested that natural aquatic humic substances were responsible for the formation of the trihalomethanes in Rotterdam drinking water, a large number of studies have concentrated on the identification and quantification of these volatile, nonpolar dissolved compounds. Although natural organic materials in water (humic acid, fulvic acid, plant extractives, etc.) are procedurally defined and of unknown and presumable diverse structural composition, a body of data exists which supports the hypothesis that they are responsible for a large fraction of the chlorinated products produced in the chlorination of drinking water.

*Department of Environmental Sciences and Engineering, School of Public Health, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27514.

In comparing the total amount of organic halogen (TOX) produced in drinking water treatment to the level of trihalomethanes (THM), Oliver (*2*) found slightly larger TOX values than THM values. Glaze et al. (*3*) found five to six times higher amounts of TOX formation potential than THM formation potential using several procedures for this comparison. These findings suggest the need for increased identification of the nonvolatile chlorination products of the OCl^-/aquatic humic reaction. Such identification was the principal objective of the work reported here and earlier by the authors (*4*) and others (*5*).

The complexity of the OCl^-/aquatic humics reaction product mixture has made it necessary to refine the separation and mass spectral identification techniques reported earlier. The refinements have resulted in a considerable increase in the range and accuracy of product identification.

Experimental

Humic Isolation and Chlorination

The isolation of humic material from the natural water system and its reaction with chlorine have been described previously (*4*). Briefly, humic acid was extracted from a highly colored surface water (Black Lake, Elizabethtown, N.C.) by acid precipitation at pH 2.2 (HCl), settling and centrifugation. After a cleanup procedure which included three rounds of redissolving in 0.5*N* NaOH, precipitation and centrifugation, the material was washed twice with pH 2.2 HCl solution and freeze-dried to a solid. For reaction with chlorine the solid material was dissolved in pH 12 NaOH solution, centrifuged and filtered for a final concentration of 420 mg/l. total organic carbon. This solution was then reacted for 48 hr at pH 12 with aqueous hypochlorite at a mole ratio (OCl^-/C) of 1.5. It is reasonable to assume that chlorination products produced at high pH do not differ qualitatively from those produced at more acidic pH values. However, greater yields of substitution products may occur at lower pH due to the increased concentration of HOCl. After this period excess chlorine was removed with sodium arsenite and the pH lowered to 1.0 with HCl. The solution was then extracted with an equal volume of redistilled diethyl ether which was then dried with sodium sulfate, concentrated in a Kuderna-Danish apparatus and methylated with diazomethane. Solvent blanks using redistilled solvent yielded no products.

GC/MS Procedures

The GC/MS facility used in these studies consists of a Hewlett-Packard 5710A capillary column gas chromatograph, interfaced to a VG Micromass 7070F double-focusing mass spectrometer equipped with a combined EI-CI source. Data reduction was performed by a VG Datasystems 2035 F/B computer and storage on Systems Industries compatible 6.6 megaword dual-density cartridge disks. A Versatec 800A electrostatic printer/plotter was used to output the data.

The gas chromatograph was fitted with a Grob-type split/splitless injector, supplied by GC^2 (chromatography) Ltd. P. O. Box 26, Northwich, Cheshire, UK. The nonpolar column used for the separations was a Hewlett-Packard 25 m SP-2100 fused-silica capillary, which was easily inserted within the 0.7 mm ID glass-lined tubing direct interface to the MS ion source as far as the quartz inlet restriction, thus eliminating most of the potential interface problems such as dead-volume or active sites. At a head pressure of 4 lb/in^2, the helium flow rate through this column was about 1 ml/min at 60°C. Analyses were also performed on a 50 m OV-17 Quadrex glass capillary column supplied by Applied Sciences, Inc. The flow rate through this column was about 0.8 ml/min at a head pressure of 10 lb/in^2. The program rate used on either column was usually 40°C/min after a 2-min delay from the injection temperature of 60°C, to a final temperature of 260°C.

The 7070F spectrometer is equipped with a Hall-probe regulated field-control system, enabling scan cycle times of around 1.2 sec. For low resolution accurate mass measurement, the cycle time was 3.0 sec over the mass range 450-20-450 (1.5 sec/decade, 1 sec interscan delay).

The standard operating conditions in EI mode were: accelerating voltage 4 kV, trap current 100 μA, electron energy 70 eV, source pressure 2×10^{-6} torr (1 ml/min helium flow), source temperature 200°C, resolution 1500. In CI mode, the reactant gas used was isobutane and the operating conditions were: filament current 500 μA, electron energy 100 eV, source pressure approximately 0.3 torr, source temperature 100°C, resolution 1000. For accurate mass measurements, a low resolution technique employing tetraiodoethylene as internal reference compound was used, enabling operation at full sensitivity.

Sample injection volumes were typically 1.5 μl, and split ratios of 5:1 to 10:1 were employed.

Bases of Structural Assignments from Mass Spectra

In general, the structure of an individual component was deduced by interpretation of the CI mass spectrum, which provided the molecular weight, and the EI accurate mass spectrum, which enabled assignment of elemental composition to the major peaks and hence the molecular formula in addition to providing a characteristic fragmentation pattern. In many cases, the identity of a component thus evaluated was confirmed by matching EI and CI mass spectra with those of an authentic standard specimen.

For example, scan #629 in the OV-17 chromatogram gave the EI spectrum shown in Figure 1. The accompanying CI spectrum indicates a compound of molecular weight 194, with the ion 31 mass units lower being indicative of a carboxylic acid methyl ester. The accurate mass of the molecular ion was determined to be 194.0568. Table 1 lists the five possible elemental formula choices for this mass within ± 10 ppm given the indicated maximum numbers of atoms for each element. Of these, only two are possible molecular ions. The others are

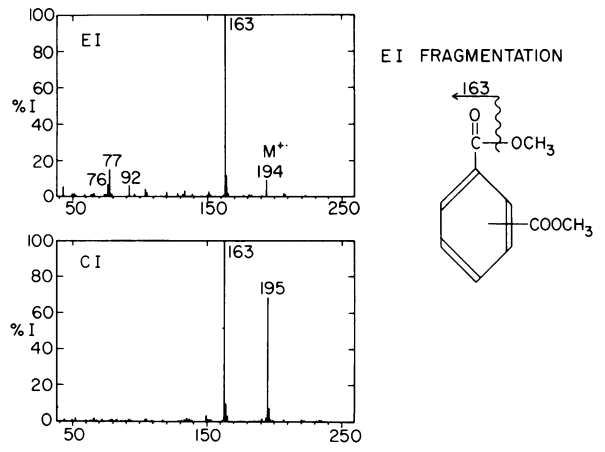

FIGURE 1. Mass spectra of a typical aromatic ester.

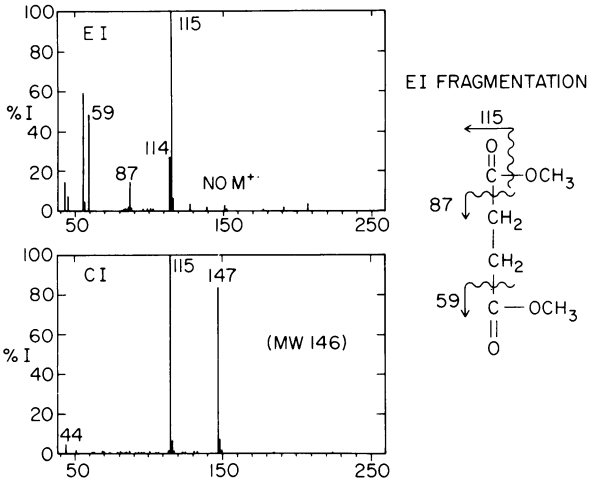

FIGURE 2. Mass spectra of a typical aliphatic ester.

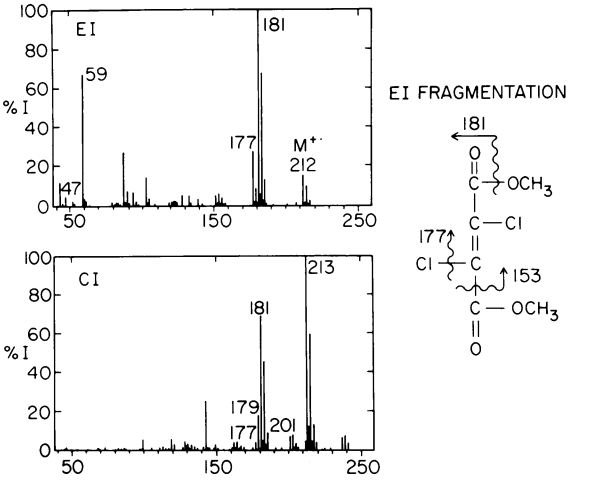

FIGURE 3. Mass spectra of a typical chlorinated ester.

eliminated either because the mass spectrum shows that there is no chlorine in the molecule or the rules of valency are not satisfied. Thus, the choice is between only two possible formulae as compared for example with thirteen possible choices when the tolerance limit is increased to 100 ppm. Even this relatively low precision is already well beyond the scope of accuracy achievable using a quadrupole spectrometer. The utility of the technique of low resolution accurate mass measurement at scan speeds compatible with capillary column GC/MS is therefore intuitively obvious. The main prerequisites for such a system are a double-focusing mass spectrometer with a highly reproducible fast cycle scan function and appropriate computer programming.

Figures 1 and 2 are examples of aromatic and aliphatic diesters which were confirmed with standard compounds. Figure 2 shows a more typical situation; no molecular ion is observed in the EI spectrum, showing the utility of the CI spectrum which usually gave an M + H ion. Having both accurate mass data and mass fragmentation patterns on compounds of similar type gives a great deal of confidence to interpretations such as that shown in Figure 3 where no standard compound or library spectrum is available.

Results and Discussion

Figure 4 shows the reconstructed gas chromatogram (RGC) of the methylated, ether-extractable, pH 12 chlorination products of aquatic humic acid analyzed with an SP-2100 fused-silica capillary col-

Table 1. Possible formulae within 10 ppm (2 mmu) for observed accurate mass 194.0568 ($M^{+\cdot}$).[a]

C	H	O	Cl	N	ppm
10[b]	10	4	0	0	-5.8
7	13	3	1	1	-8.3
8	8	3	0	3	1.1
5	11	2	1	4	-1.4
6[b]	6	2	0	6	8.0

[a]Given: $^{12}C/40$, $^{16}O/9$, $^{35}Cl/6$, $^{14}N/6$.
[b]Chemically feasible choices; possible formulae within 100 ppm total 37, of which 13 are chemically feasible.

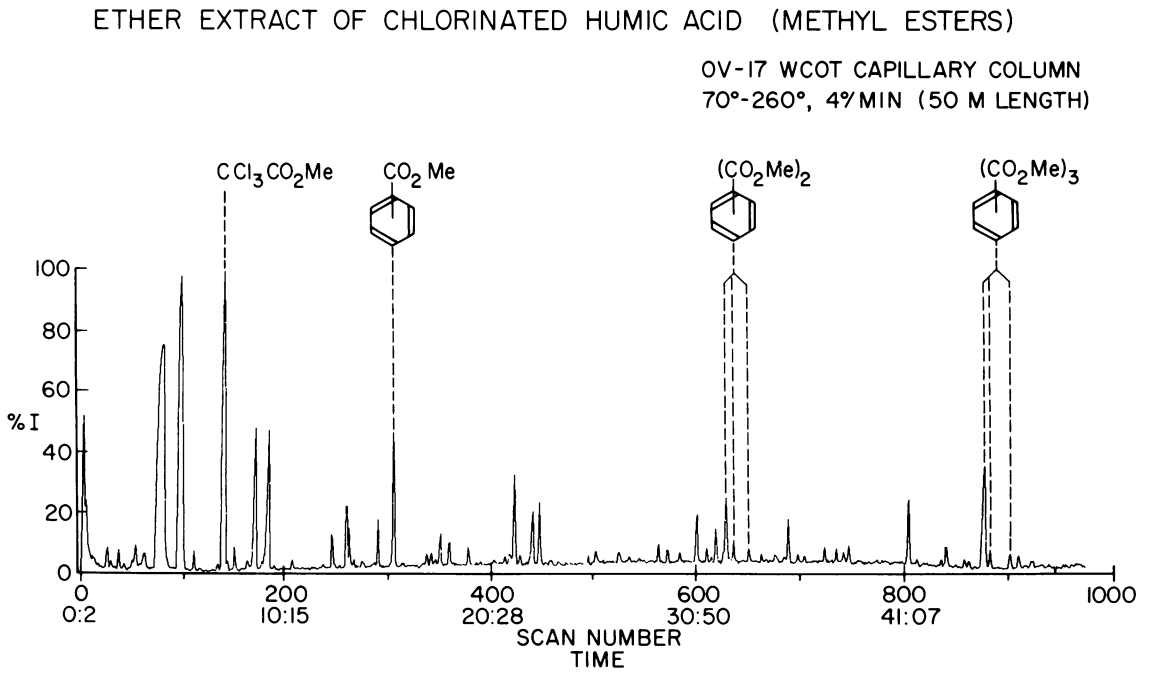

FIGURE 4. Reconstructed gas chromatogram of the methylated, ether-extractable, pH 12 chlorination products of aquatic humic acid analyzed with an SP-2100 fused-silica capillary column.

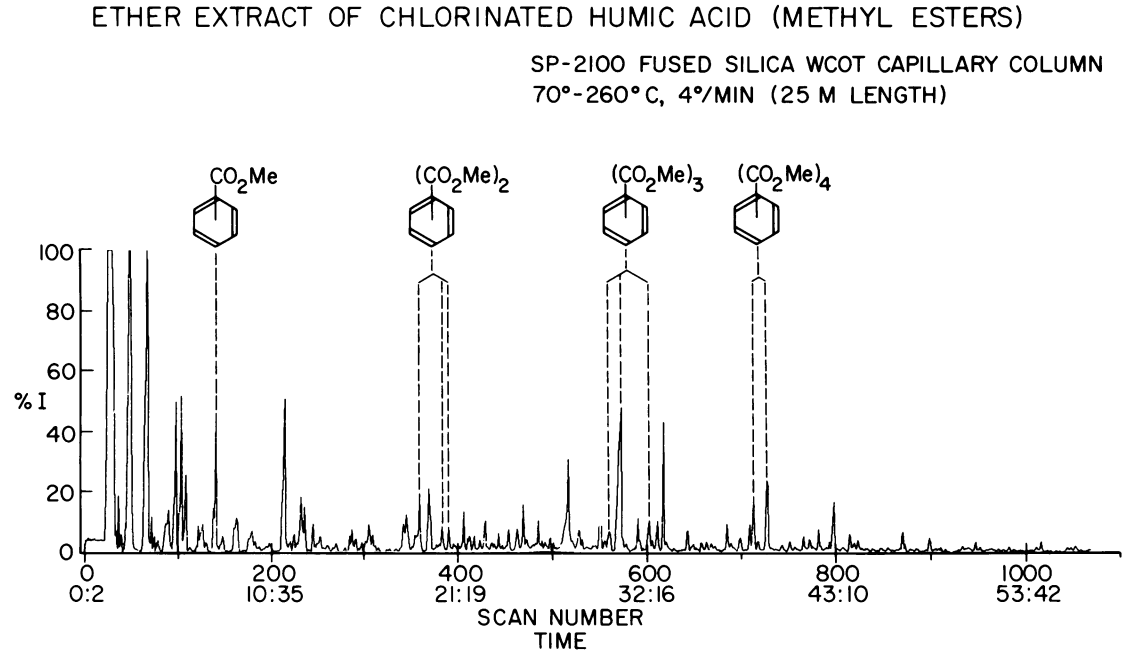

FIGURE 5. Reconstructed gas chromatogram of the methylated, ether-extractable, pH 12 chlorination products of aquatic humic acid analyzed with an OV-17 glass capillary column.

Table 2. Summary of components detected by GC/MS.

Type of compound	Number of compounds and method[a]	
	Packed	Capillary
Aliphatic monoesters	5 (1)	21 (1+2)
Aliphatic diesters	5 (1)	11 (1+2)
Aromatic esters	15 (1)	24 (1+2)
Chlorinated compounds	15 (1)	15 (1), 36 (2)
Others	0 (1)	38 (2)

[a](1) = OV-17; (2) = SP-2100.

umn. In the original packed column results (*4*), approximately 8% of the starting carbon appeared as chromatographable products. With the technique used it is not possible to analyze extremely low molecular weight materials such as haloforms or the high molecular weight, neutral or basic fractions, or other components nonextractable into ether from acid solution or nonchromatographable. In addition to the experimental advantages of the fused-silica capillary column, the 25 m column using the SP-2100 coating (Fig. 4) gave a wider boiling range of identified products than a 50 m glass capillary OV-17 column (Fig. 5). The latter column, however, gave better separations and both capillary columns produced much better results than those reported in the previous study (*4*) with the use of OV-17 with a packed column. For instance, the first of the dicarboxybenzoic acids in scan #359 in Figure 4 was not resolved from the next higher molecular weight material in the original packed column data. This dicarboxybenzoic acid, even with the SP-2100 fused-silica column, has a small unresolved shoulder. The extremely high performance of the OV-17 glass capillary column is clearly shown, as the first dicarboxybenzoic acid is completely resolved as a single component (scan #629 in Fig. 5).

Table 2 gives a summary of the number of components detected by each of the three chromatographic systems. The SP-2100 column with its wider boiling range separation eluted a larger number of compounds than the OV-17 column. The higher molecular weight materials above scan #600 only seen with the SP-2100 column were, however, in rather small yield.

Nearly all of the products identified in this experiment are esters presumably derived from the methylation of mono- and polybasic acids. These include mono- and dibasic, saturated and unsaturated, chlorine substituted and unsubstituted acids. In especially high yield are di- and trichloroacetic acid, dichlorosuccinic acid, and a series of isomers including dichloromaleic acid. A large number of mono- and dibasic unchlorinated aliphatic acids from acetic and oxalic acid up to the C_{27} monobasic fatty acid were identified. The dibasic unchlorinated aliphatic acids were generally low molecular weight containing from 2 to 10 carbons. The aliphatic acids may be ring-cleavage products. Most are also in relatively low yield indicated by one or two stars in the "Relative abundance" column shown in Tables 3 and 4. Aromatic acids including mono- to hexacarboxybenzoic acid in all isomers as well as small quantities of methyl-substituted aromatic acids and isomers of carboxyl-substituted α-ketobenzoic acid were also detected. Noticeably missing from the aromatic series are chlorine-substituted aromatic acids and aromatic acids with aliphatic side chains other than methyl. This pattern is similar to that found with permanganate oxidation, suggesting that chlorine in alkaline solution is capable of oxidizing side chains down to terminal carboxyl groups on the aromatic ring.

The products found in this study are similar to those previously identified (*4*), but as shown in Table 2, a significant number of additional compounds are reported here. In addition, the separation of multicomponent peaks made possible by capillary gas chromatography has also improved the accuracy of the mass measurements made, providing more confidence in the elemental formulae assigned and structures determined.

Summary and Conclusions

Tables 3 and 4 list the assignments made for the chromatograms shown in Figures 4 and 5. Along with the proposed structure or elemental formula, a scan number is listed for reference back to Figures 4 and 5 as well as the relative abundance. The highest or most abundant yield of product is shown as five stars down to the lowest or least abundant yield as a single starred component. Also listed are comments as to confidence in assigned structure and other comments. The phrase "standard confirmed" notes those compounds in which authentic standards have been used to confirm structures.

The relatively high yields of di- and trichloroacetic acid, although they are quite low in molecular weight, extremely acidic and polar, making their extraction into ether relatively inefficient, would suggest that

Table 3. Chlorination products identified on SP-2100.

Proposed structure or formula	Scan number	Relative abundance	Comments
C_2HOCl_3	34	***	Possible solvent impurity
$ClCH_2—COOCH_3$	37	***	Confident
Aliphatic	39	**	Possible solvent impurity
$Cl_2CH—COOCH_3$	46	*****	Standard confirmed
Unknown	51	***	Possible solvent impurity
$Cl_3C—COOCH_3$	64	*****	Standard confirmed
$Cl_2C = CH—COOCH_3$ (isomer)	72	**	Tentative
$C_3H_5O_2Cl$	74	*	Tentative
Unknown	75	**	
$Cl_2C = CH—COOCH_3$ (isomer)	77	*	Isomer of 72, tentative
Ar—COH	79	*	Confident
Dichlorinated ester	85	*	Tentative
$Cl_3C—COH$	88	*	Tentative
$C_5H_7O_2N$	90	***	Tentative
Unknown aliphatic compound	95	**	
Unknown aliphatic compound	97	***	
Unknown aliphatic compound	101	**	
Unknown aliphatic compound	104	*****	
$H_3COOC—(CH_2)_2—COOCH_3$	108	***	Standard confirmed
$C_3H_4O_2Cl_2$	122	*	Tentative
Aliphatic diester	125	*	Tentative
Monochlorinated aliphatic diester	127	*	Tentative
Unknown	130	*	
$Ar—COOCH_3$	138	***	Standard confirmed
Chlorinated aliphatic ester	145	*	Tentative
Dichlorinated aliphatic compound	148	*	Tentative
$H_3COOC—CH = CCl—COOCH_3$ (isomer)	153	*	Tentative
$H_3COOC—CH_2—CHCl—COOCH_3$	160	*	Confident
$H_3COOC—CH_2—CHCl—COOCH_3$	163	**	Isomer of 160, tentative
Aliphatic diester	176	*	Tentative
Aliphatic diester	180	***	Tentative
Aliphatic ester	183	*	Tentative
Unknown	197	*	
Dichlorinated aliphatic ester	213	***	Tentative
$H_3COOC—C_2H_2Cl_2—COOCH_3$ (isomer)	215	*****	Tentative
$H_3C—(CH_2)_7—COOCH_3$	221	*	Confident
Trichlorinated aliphatic ester	224	*	Tentative
$H_3COOC—CCl = CCl—COOCH_3$	230	*	Isomers, *cis* and *trans*
	232	**	
Tetrachlorinated aliphatic ester	245	*	Tentative
Unknown	247	*	
Unknown	252	*	
Aliphatic diester	260	*	Tentative
Aliphatic diester	270	*	Tentative
$H_3C—(CH_2)_8—COOCH_3$	284	*	Tentative
$Ar—CHCl—COOCH_3$	287	**	Tentative
$H_3COOC—(CH_2)_5—COOCH_3$	291	*	Confident
$C_7H_8O_4Cl_2$ aliphatic ester	297	*	Tentative
Dichlorinated aliphatic ester	305	*	Tentative
Dichlorinated aliphatic aldehyde or ketone	309	**	Tentative
$C_8H_{10}N_2O_4$	342	**	Very tentative, note homologs at 510, 513, 516
	345		
$H_3COOC—(CH_2)_6—COOCH_3$	354	*	Confident
$Ar—(COOCH_3)_2$	359	****	Standard confirmed
Trichlorinated aliphatic ester	369	**	Tentative
Chlorinated ester	371	*	Tentative
Aliphatic ester	377	*	Tentative
$Ar—(COOCH_3)_2$ + chlorinated compound	383	*	Standard confirmed
$Ar—(COOCH_3)_2$	389	*	Standard confirmed
$H_3C—Ar—(COOCH_3)_2$	404	*	Tentative
$H_3C—(CH_2)_{10}—COOCH_3$	406	**	Confident
Aliphatic diester	410	*	Tentative
Chlorinated aliphatic diester	413	*	Tentative
$C_8H_8O_5$	417	*	Tentative
Aliphatic ester	428	*	Tentative
Ester	429	*	Tentative

Table 3. *(Continued)*

Proposed structure or formula	Scan number	Relative abundance	Comments
$C_6H_{11}O_3Cl_4$ ester	439	*	Tentative
$H_3C—(CH_2)_{11}—COOCH_3$	443	*	Confident
$C_8H_8O_5$	454	**	Homolog of 417, tentative
Chorinated ester	462	*	Tentative
$H_3C—(CH_2)_{11}—COOCH_3$ + chlorinated ester	463	*	Confident
$C_9H_7O_2Cl_5$ ester + $C_8H_9O_6Cl$ ester	469	**	Tentative
Isomer of 345	474	*	Tentative
$C_6H_8O_3Cl_4$ ester	482	*	Tentative
Aliphatic ester	485	*	Tentative
Aliphatic monoester	489	*	Tentative
Unknown mixture	492	*	
$H_3C—(CH_2)_{12}—COOCH_3$	497	*	Confident
$C_7H_8N_2O_4$	510	*	Homologs of 342, 345, 474, tentative
	513	**	
	516	***	
$H_3C—(CH_2)_{12}—COOCH_3$	517	***	Confident
$C_{12}H_{13}O_4Cl_3$	523	*	Tentative
Complex aliphatic ester	528	*	Tentative
$C_{11}H_{12}O_3Cl_4$ ester	523	*	Tentative
Aliphatic monoester	543	*	Tentative
$H_3C—(CH_2)_{13}—COOCH_3$	550	**	Confident
$Ar—(COOCH_3)_3$ + another aromatic	558	*	Standard confirmed
$Ar—(COOCH_3)_3$	566	***	Standard confirmed
$C_{10}H_9O_4Cl_3$ ester	577	*	Tentative
Complex aliphatic ester	589	**	Tentative
$Ar—(COOCH_3)_3$	601	**	Standard confirmed
$C_8H_9O_5Cl_3$ ester	604	*	Tentative
$H_3C—Ar—(COOCH_3)_3$ + complex chlorinated ester	610	*	Tentative
$H_3C—(CH_2)_{14}—COOCH_3$	616	****	Confident
Complex aliphatic compound	619	*	Tentative
$H_3COOCOC—Ar—(COOCH_3)_2$	641	**	Very tentative
$C_{11}H_9O_5Cl_3$ ester	647	*	Tentative
$C_{12}H_8O_5Cl_2$ ester	651	*	Tentative
$C_{12}H_{10}O_2Cl_4$ ester	657	*	Tentative
Mixture of esters	662	*	Tentative
$H_3C—Ar—(COOCH_3)_3$ + another compound(s)	666	*	Tentative
Complex aliphatic compound	684	**	Tentative
$H_3COOCOC—Ar—(COOCH_3)_2$ + $H_3C—Ar—(COOCH_3)_3$	688	*	Very tentative
$Ar—(COOCH_3)_4$	697	*	Standard confirmed
$H_3C—(CH_2)_{16}—COOCH_3$	708	*	Confident
$Ar—(COOCH_3)_4$	712	***	Standard confirmed
Aliphatic diester	716	*	Tentative
$Ar—(COOCH_3)_4$	726	****	Standard confirmed
$(H_3C)_2—Ar—(COOCH_3)_3$	750	*	Tentative
$H_3COOCOC—Ar—(COOCH_3)_3$	764	*	Very tentative
Complex aliphatic compound	771	*	Tentative
$H_3COOCOC—Ar—(COOCH_3)_3$	781	**	Very tentative
$H_3C—(CH_2)_{18}—COOCH_3$	792	*	Confident
$H_3COOCOC—Ar—(COOCH_3)_3$	797	***	Very tentative
$H_3COOCOC—Ar—(COOCH_3)_3$	814	*	Very tentative
$Ar—(COOCH_3)_5$	822	*	Standard confirmed
Phthalate	869	*	Confident
$H_3C—(CH_2)_{20}—COOCH_3$	871	*	Confident
$H_3COOCOC—Ar—(COOCH_3)_4$	883	*	Very tentative
$H_3COOCOC—Ar—(COOCH_3)_4$	897	*	Very tentative
$H_3C—(CH_2)_{21}—COOCH_3$	909	*	Confident
$C_{18}H_{16}O_8$ ester	932	*	Tentative
$H_3C—(CH_2)_{22}—COOCH_3$	946	*	Confident
$C_{18}H_{16}O_8$ ester	950	*	Tentative
$H_3C—(CH_2)_{23}—COOCH_3$	981	*	Confident
$H_3C—(CH_2)_{24}—COOCH_3$	1015	*	Confident
$C_{20}H_{18}O_{10}$ ester	1043	*	Tentative
$C_{20}H_{18}O_{10}$ ester + $H_3C—(CH_2)_{25}—COOCH_3$	1051	*	Tentative, confident

Table 4. Chlorination products identified on OV-17.

Proposed structure or formula	Scan number	Relative abundance	Comments
$ClCH_2—COOCH_3$	53	**	Confident
$H_3C—COOC_2H_5$	80	*****	Solvent
$Cl_2CH—COOCH_3$	96	*****	Standard confirmed
$H_3COOC—COOCH_3$	110	**	Confident
Unknown	134	*	Related to 143, 171, 183
$Cl_3C—COOCH_3$	137	*****	Standard confirmed
Unknown	143	*	Related to 134, 171, 183
$Cl_2C—CH—COOCH_3$ (isomer) + $H_3C—COOCH_2Cl$	150	**	Tentative
$H_3COOC—CH_2—COOCH_3$	162	*	Confident
Unknown	171	*****	Related to 134, 143, 183
$Cl_3C_2H_2—COOCH_3$	176	*	Very tentative
Unknown	183	*****	Related to 134, 143, 171
$Ar—COH$	207	*	Confident
$Cl_2C—C_3H_7—COOCH_3$	245	**	Tentative, isomers
$H_3COOC—(CH_2)_2—COOCH_3$	259	***	Standard confirmed
$C_5H_7NO_2$	262	**	Tentative
$H_3C(Cl)C—(COOCH_3)_2$ or $ClH_2C—CH—(COOCH_3)_2$	290	***	Tentative
$Ar—COOCH_3$	305	*****	Standard confirmed
$H_5C_2—CH—(COOCH_3)_2$	337	*	May be interchanged with 341, tentative
$H_3COOC—CH_2—CH(CH_3)—COOCH_3$	341	*	May be interchanged with 337, tentative
$H_3COOC—CH_2—CHCl—COOCH_3$ + another methyl ester	351	**	Confident
$H_3COOC—CCl_2—COOCH_3$	360	**	Confident
$H_3COOC—(CH_2)_3—COOCH_3$	378	**	Confident
$H_3COOC—CCl_2—CH_2—COOCH_3$	423	****	Tentative
$H_3COOC—(CH_2)_4—COOCH_3$	428	**	Confident
$H_3COOC—CCl=CCl—COOCH_3$	441	**	Isomers, *cis* and *trans*
	447	***	
$H_3COOC—(CH_2)_5—COOCH_3$	503	**	Confident
$Cl—C_7H_6—COOCH_3$	525	**	Isomers, tentative
	535	**	
$H_3C—(CH_2)_{10}—COOCH_3$	564	**	Confident
$H_3COOC—(CH_2)_6—COOCH_3$	572	**	Confident
$[C_3H_2Cl_2O]—(COOCH_3)_2$	584	**	Very tentative
$C_{13}H_{10}O_2$ or $C_8H_{10}N_2O_4$	601	***	Tentative
$Ar—(COOCH_3)_2$	629	****	Standard confirmed
$Ar—(COOCH_3)_2 + H_3COOC—(CH_2)_7—COOCH_3$	636	*	Standard confirmed
$Ar—(COOCH_3)_2$	651	**	Standard confirmed
$H_3C—(CH_2)_{12}—COOCH_3$	688	*	Confident
$H_3COOC—(CH_2)_8—COOCH_3$	698	*	Confident
$H_3C—Ar—(COOCH_3)_2$	704	*	Tentative
$H_3C—(CH_2)_{13}—COOCH_3$	724	*	Isomers, confident
	730	*	
	747	*	
$H_3C—(CH_2)_{14}—COOCH_3$	805	***	Confident
$C_{14}H_{12}O_2$	840	**	Possible artifact
$Ar—(COOCH_3)_3$	878	*****	Standard confirmed
$Ar—(COOCH_3)_3$	883	**	Standard confirmed
$Ar—(COOCH_3)_3$	902	*	Standard confirmed
$H_3C—(CH_2)_{16}—COOCH_3$	910	*	Confident

these compounds are major products of the chlorination of aquatic humic materials. These compounds, because of their concentration, are likely candidates for additional toxicology and mutagenicity testing. It is important to note that chlorinated aromatic structures which are commonly found in toxic materials are completely absent from the structures identified in this study.

Three major factors in the analytical procedure employed were crucial to the success of the compound identifications. These are: (1) the use of fused-silica capillary GC columns with their flexibility and high separation efficiency; (2) the ability to employ scan rates compatible with the sharp elution profiles of the GC peaks using a double-focusing sector mass spectrometer and; (3) the acquisition of accurate mass data without serious compromise to the sensitivity or scan speed. Item three results from the fact that low resolution was employed in these analyses. If high resolution had been used,

sensitivity would have suffered, and scan rates would have had to be slower to obtain an undistorted spectrum. This is incompatible with the very sharp peaks eluting from capillary columns. Compared with the typical nominal mass data obtained with quadrupole spectrometers and the use of library search techniques, we are able to identify many more components with a much greater degree of certainty.

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